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INVESTIGATION OF NICKEL - SILICON METALLIZATION PROCESS

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FINAL REPORT

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SECTION 1.0

ABSTRACT

The metallization of silicon solar cells passivated with silicon nitride coating was investigated by using commercial Ni pastes # 5517 from Thick Film Systems, # 7028-5 from Cermalloy. experimental formulation # X-A by Sollos, Inc. and evaporated Ti-Ni film.

Comparative and reference tests were done with the Dupont Ag paste # 7095 and with a mixture of Ni paste # 5517 with Ag paste # 7095 in the respective ratio of 9 to 1 by weight.

The evaluation criteria for the metallization were the mechanical bond strength of the contact, solderability, copper plating ability and electrical characteristics in terms of Voc, Isc values and shape of the V-I curve.

The results revealed that the Dupont Ag paste # 7095 met all required criteria, while the quality of the cells metallized with the commercial Ni paste # 5517 from Thick Film Systems, # 7028-5 from Cermalloy as well as the experimental paste # X-A from Sollos, Inc. was below the acceptable standards.

A significant improvement was obtained with the mixture of Ni paste # 5517 from Thick Film Systems with 10% addition of Dupont paste # 7095.

Optimized ratio of the mixture of these two pastes was not determined due to the time limit allocated for this work and should be subjected to further studies.

SECTION 2.0

INTRODUCTION

The objectives of this program were to investigate the metallization process for silicon PV cells, based on Ni screenable pastes and applied on silicon nitride coated wafers.

The problems associated with this task were complex due to requirements imposed on the Ni paste compositions perse and by the interaction of the Ni paste with the nitride coating.

With regards to the Ni paste composition, the firing temperature of the paste may not exceed 700°C in order to prevent electrical shorts and the binder must be active at this temperature.

Furthermore, this binder must also react with the nitride coating to facilitate the contact between the silicon and nickel.

Finally the resulting Ni film must be solderable either directly by lead-tin solder or by the conditioning of the Ni surface to accept the solder by means of copper plating.

The approach to study this process within the 5 months time span was based on a series of experimental tests using two commercial Ni pastes, i.e. product # 5517 from Thick Film Systems and # 7028-5 from Cermalloy.

The purpose of these tests was to evaluate the quality of the metallization in terms of mechanical bond, solderability and electrical characteristics, i.e.Voc, Isc and V-I curve and to determine the dependence of the quality of the cells on temperature and atmosphere of the metallization process.

In order to isolate various variables introduced by the use of Ni pastes on the nitride coating, reference tests were done with evaporated Ti-Ni films and with

the Dupont Ag paste # 7095.

The purpose of the tests done with the thin film Ti-Ni metallization was to determine the effect of the binder present in the thick film Ni paste in contrast with its absence in the evaporated film.

The Ag paste # 7095 from Dupont on the other hand served the purpose to establish the difference between the Ag and Ni as the contacting metals.

Finally, an initial test using both thick film Ni paste # 5517 from Thick Film Systems mixed with 10% Ag paste # 7095 from Dupont was evaluated.

The details of the experimental data is presented in the technical discussion.

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SECTION 3.0

TECHNICAL DISCUSSION

3.1 Experiments with Ti-Ni thin film metallization.

Diffused 2 inch diameter silicon wafers were provided for this test by the JPL.

The diffusion depth from the $POCl_3$ source was .43 microns.

A group of nitride coated junctions (800-850 Å thick film) had on the active side a contact pattern obtained by evaporation of 400 Angstroms thick titanium and 2000 - 3000 Angstroms thick nickel film. *

A group of cells (second group) had evaporated pattern of Ti-Ni films, as the previous samples, but without the nitride coating.

The structure of the cells in individual groups is shown in fig. 1 and fig. 2

The objective was to establish the contact characteristics of pure Ti-Ni systems on nitride coated as well as uncoated wafers and the interaction of the Ti-Ni system with the silicon nitride coating at elevated temperatures and various atmospheres.

In the first group of experiments, uncoated wafers with the front contact pattern were screened with Al fritless ink (Electrink # ALF-40) on the backside and were subjected to a heat treatment of 750° C for 30 seconds in air.

As a result of this treatment the P/N junction was shorted in the metallized region.

In addition to this, the Ti-Ni metallization was not solderable in contrast with the ease of soldering to the samples which were notsubjected to the heat treatment.

* Titanium was elected instead of Chromium originally proposed due to proven experience with Ti in Si solar cell metallization

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In the second group of experiments the silicon nitride wafers with the front contact pattern were coated on the back side with Al ink (Electrink # ALF-40) and subjected to the identical treatment as the uncoated samples. In this second case the Al did not alloy with the silicon and the Ti-Ni metallization did not short the junction.

The Ni however again refused to accept the solder and this condition developed after the heat treatment in air as well as in nitrogen atmosphere.

The results of the tests are listed in table I.

THIN FILM Ti-Ni METALLIZATION STRUCTURE.

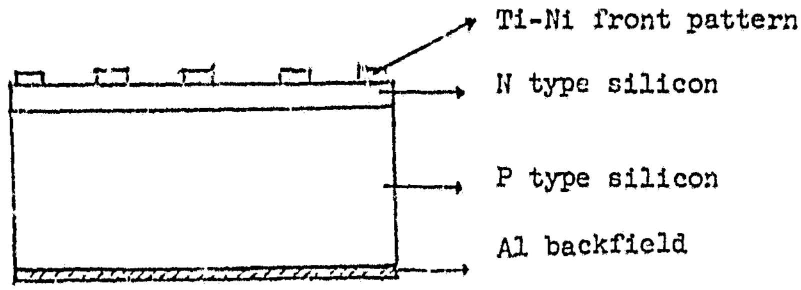


Figure 1

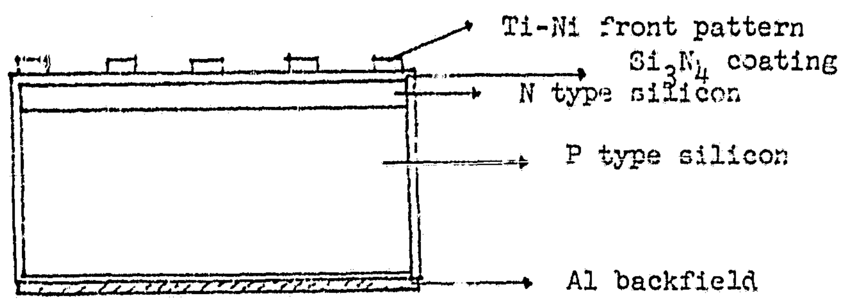


Figure 2

THIN FILM Ti-Ni METALLIZATION DATA -- TABLE 1

Structure	Al backfield temp.	Voc(V)	Isc(mA)	solderability	Cu plating
N-P uncoated (Si_3N_4)	750°C-30 sec (nitrogen)	short	--	no	no
N-P coated (Si_3N_4)	750°C-30 sec (nitrogen)	.52-.54	10	no	no

3.2 Experiments with thick film nickel pastes.

The thick film Ni pastes used in these tests were # 5517 purchased from Thick Film Systems, paste # 7028-5 from Cermalloy and experimental paste # X-A from Sollos, Inc.

In all experiments the cells had a back surface field formed by firing fritless Al ink (Electrink # ALF-4C) at 750° C for 30 seconds in air.

Through experiments with nickel pastes was established that the firing cycle has to have the peak temperature below 700° C in order to prevent shorting.

Also observed was that the firing time at this temperature was very critical.

A one-minute heat treatment at 690° C in air resulted in an open circuit voltage of .55 V and a short circuit current of 20 mA.

An additional two-minute heat exposure at 690° C in air improved the short circuit current to 95 mA, but degraded the open circuit voltage to .345 V.

The preliminary explanation of this characteristic was that the flux present in the nickel paste had removed the nickel oxide formed during the heat cycle and that the relatively good conductive nickel coating was obtained in the short firing time.

By longer exposure however, the nickel re-oxidized since the flux, added in the paste, was already depleted.

This mechanism was further supported by experiments done with the nickel paste in nitrogen atmosphere.

The initial tests showed that the open circuit voltage under this condition was .54 V and the short circuit current about 300 mA.

Wafers metallized with nickel paste fired at 650° C for one minute in nitrogen atmosphere resulted in open circuit voltage of .45 - .47 V and short circuit current of 120 - 150 mA.

These values did not change by an additional one-minute heat treatment at 650° C.

The metallization seemed to have a good adherence, but was not solderable with lead-tin solder.

An attempt to deposit copper by a plating process from copper sulphate was not successful since the bond of nickel to silicon was destroyed by the immersion of the wafers in the plating solution.

Also an attempt to obtain the solderable nickel by a short immersion in diluted hydrofluoric acid was not successful.

The structure of the cells metallized with Ni pastes is in fig. 3 , a typical V-I characteristic of thick film Ni metallization in fig. 4 and collective data are presented in table II.

Composition of experimental Ni paste # X-A from Sollos, Inc.

In order to lower the firing temperature of the nickel metallization, a new composition was formulated using as a binder glass melting at 450° C. This glass was obtained from Johnson Mathey in the form of a paste, type LCD, # 060123.

Ni powder in the composition was Sheritt & Gordon Mines, product N F - 1 M.

The vehicle used in the paste formulation consisted of (in weight procents):

75% TCE
15% Ethylcellulose
8% Carbitol solvent
2% Carbitol acetate

10 Grams Ni powder with 5 grams vehicle and 2 grams glass paste were mixed together.

THICK FILM Ni PASTE METALLIZATION STRUCTURE

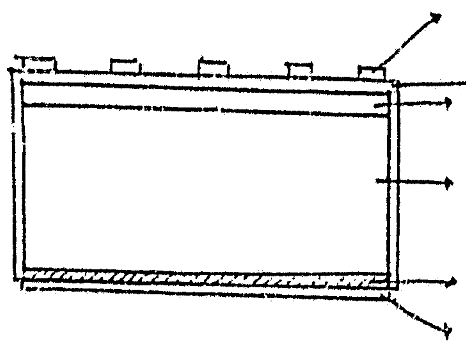


Figure 3

THICK FILM Ni PASTES METALLIZATION DATA-- TABLE 2

Paste type	Voc(V)	Isc(mA)	Solderability	Cu plating
TFS 5517	.45-.47	120-150	no good	no
Cermalloy 7028-5	.42-.47	100-130	no good	no
Sollos X-A	.45-.48	120-160	no good	no

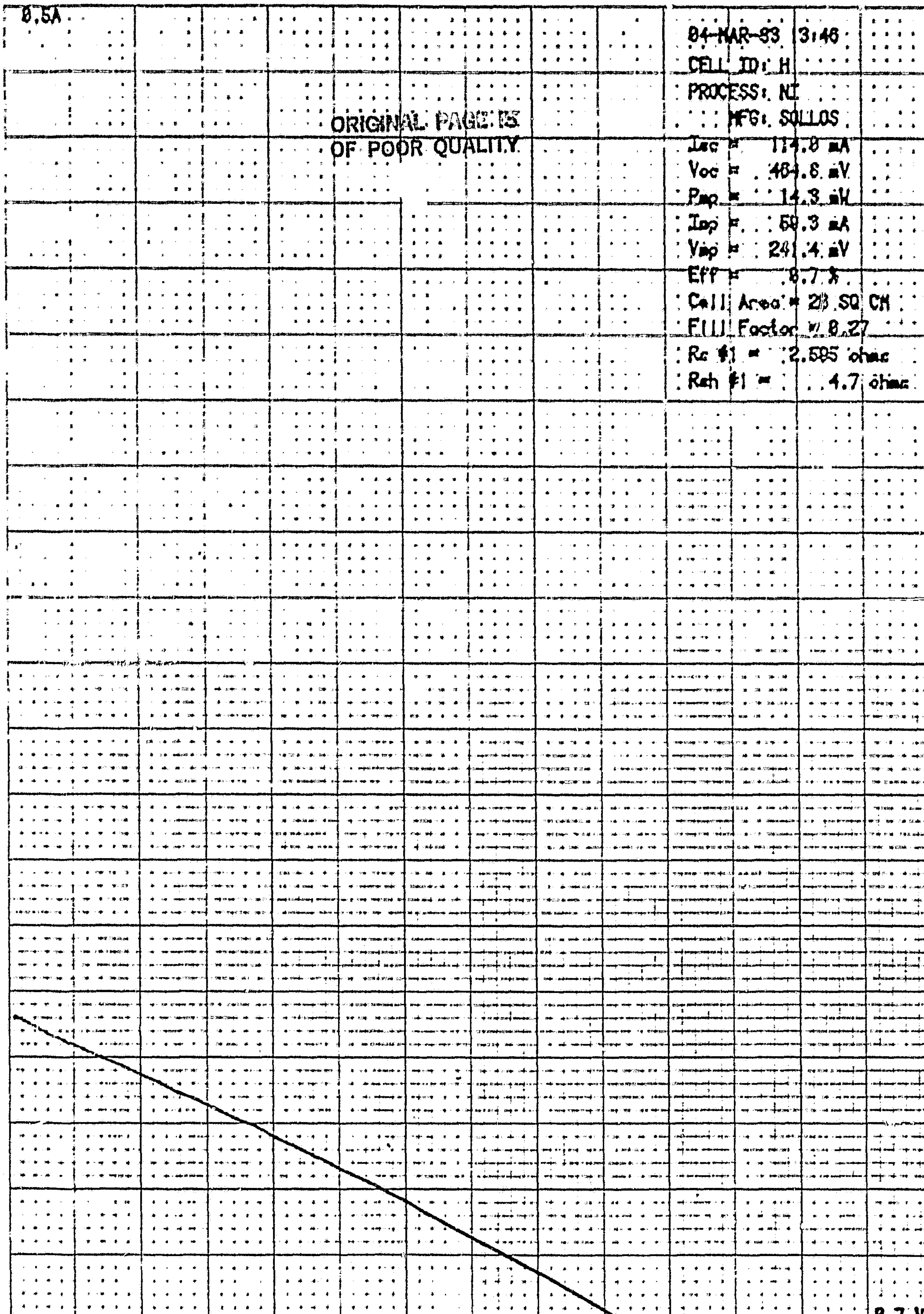

0.5A
04-MAR-83 3:46
CELL ID: H
PROCESS: NI
MFG: SOLLOS
Isc = 114.0 mA
Voc = 464.6 mV
Pmp = 14.3 mW
Imp = 59.3 mA
Vmp = 241.4 mV
Eff = 8.7 %
Cell Area = 23 SQ CM
Fill Factor = 0.27
Rs #1 = 2.585 ohms
Rsh #1 = 4.7 ohms
0.7 V

fig. 4

3.3 Experiments with the silver paste # 7095 from Dupont.

Diffused 2 inch diam. wafers from the JPL, coated with 800-850 Å Si_3N_4 film and Dupont Ag paste # 7095 were used in these tests.

The wafers were prepared in a similar fashion as in the Ni paste tests, i.e. the silicon nitride coating from the backside was removed by polishing and aluminum fritless ink (Electrink # ALF-40) was screened on the back side and fired in air at 750° C for 30 seconds.

Both back and front sides of the cells have been screened with # 7095 Dupont ink.

These samples were fired in air and two different temperature cycles were used.

In the first experiments firing at 750° C for one minute was employed.

The open circuit voltage and the short circuit current resulting from this cycle were in the range of .54 - .57 V and 450 - 550 mA.

The back side of the wafers however showed dark regions of aluminum penetrating through the silver metallization.

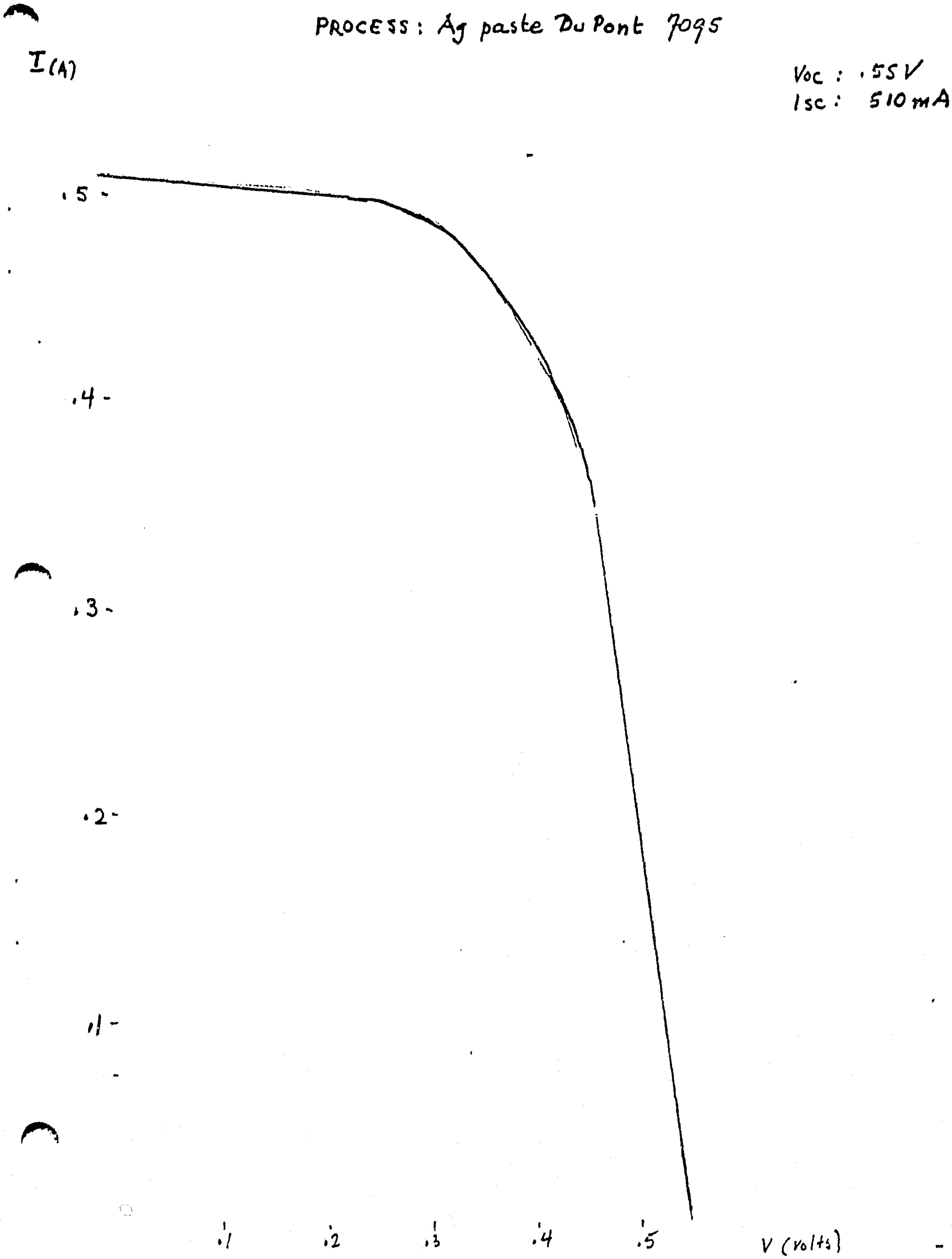
These regions were not solderable with lead-tin solder.

Therefore, in the second experiment, the silver metallized wafers were fired at 650° C for one minute in air.

The results of the open circuit voltage and the short circuit current values were in the same range as the wafers fired at 750° C, while the back side maintained a solderable, undisturbed silver metallization.

In can be concluded - so far - that the Dupont silver # 7095 can be used successfully on the silicon nitride coated wafers when the aluminum backfield is employed and silver firing temperature is done at 650° C - one minute firing cycle.

A typical V-I characteristic of the thick film silver metallization is shown on fig. 5


PROCESS: Ag paste Du Pont 7095
I (A)
Voc : .55V
Isc : 510mA
.5
.4
.3
.2
.1
.1
.2
.3
.4
.5
V (volts)

3.4 Modification of the Ni paste # 5517 from Thick Film Systems.

Three types of tests were done in this direction.

a) Addition of Dupont Ag paste # 7095 to the Ni paste TFS # 5517.

10% Ag paste was added to the Ni paste and screened on both sides of the cells which had aluminum backfield metallization formed by firing of fritless aluminum at 750° C for 30 seconds in air. (Electrink ALF-40) The metallized cells were fired in nitrogen atmosphere at 650° C for one minute.

The resulting cells had an open circuit voltage between .52 - .54 V and a short circuit current between 250 - 350 mA.

The typical curve of these types of cells is shown on the attached fig. # 6

These cells had a shunt resistance of around 2 ohms and series resistance of about 1.8 ohms.

b) Addition of 60% tin and 40% lead solder paste to the thick film Ni.(TFS # 5517)

In these tests 10% tin-lead solder paste was added to the thick film paste and the firing was done in the same manner as described in the previous tests.

Here the result did not show any difference from the characteristics obtained by the use of straight Ni paste.

c) In a reference test a group of cells was made with the thick film Ni, # 5517 TFS paste screened on the backside of the cells and Dupont Ag paste # 7095 on the active side.

The structure is shown in fig. 7

These cells had an open circuit voltage of about .53 V and a short circuir current of about 370 mA.

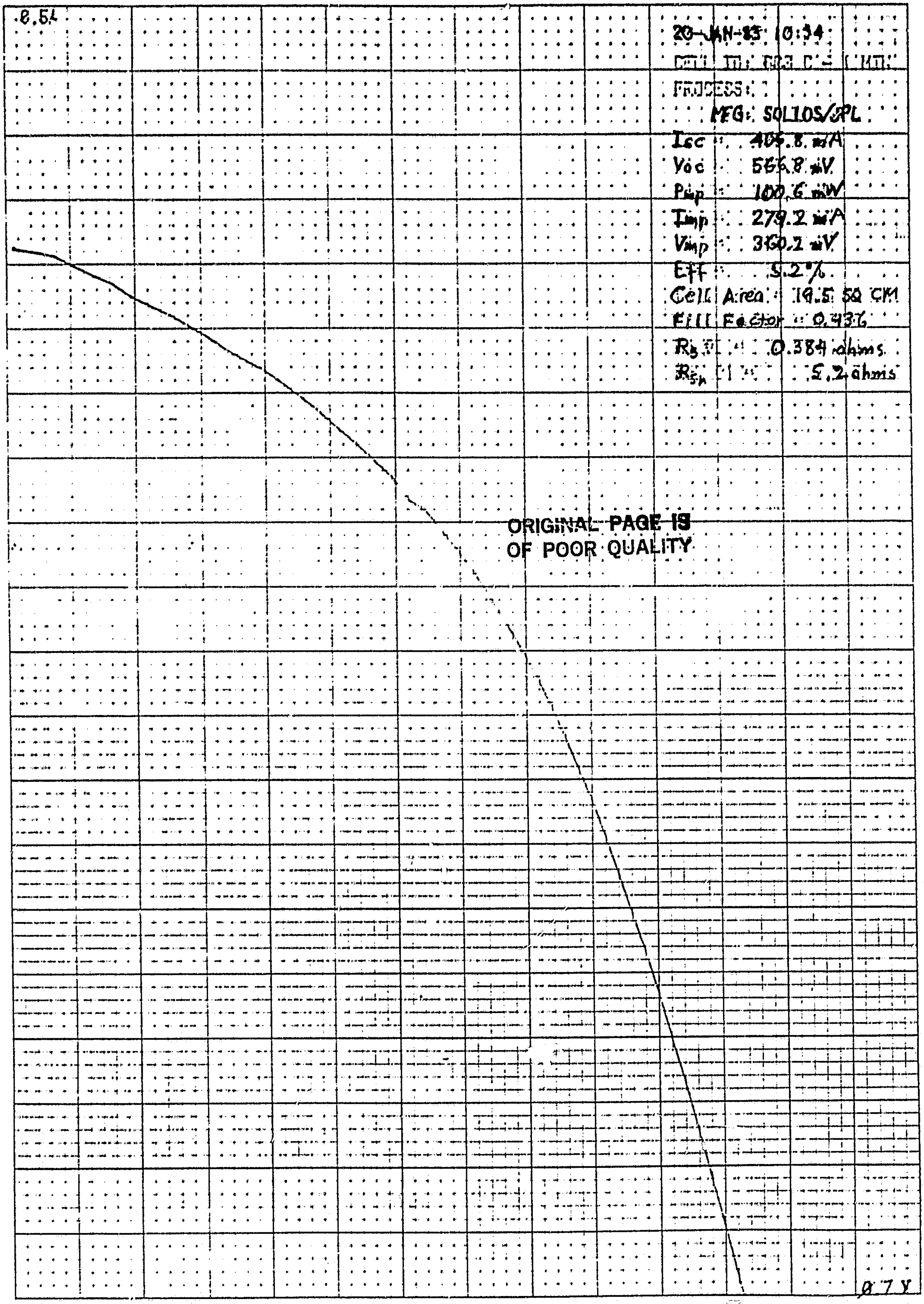

0.5A
20-JAN-83 10:34
PROCESS:
MFG: SOL10S/SPL
Isc : 405.8 mA
Voc : 566.8 mV
Pmp : 100.6 mW
Imp : 279.2 mA
Vmp : 360.2 mV
Eff : 5.2%
Cell Area : 19.5 SQ CM
Fill Factor : 0.436
Rs : 0.384 ohms
Rsh : 5.2 ohms
0.7V

fig. 6

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THICK FILM Ni - THICK FILM Ag COMBINED STRUCTURE

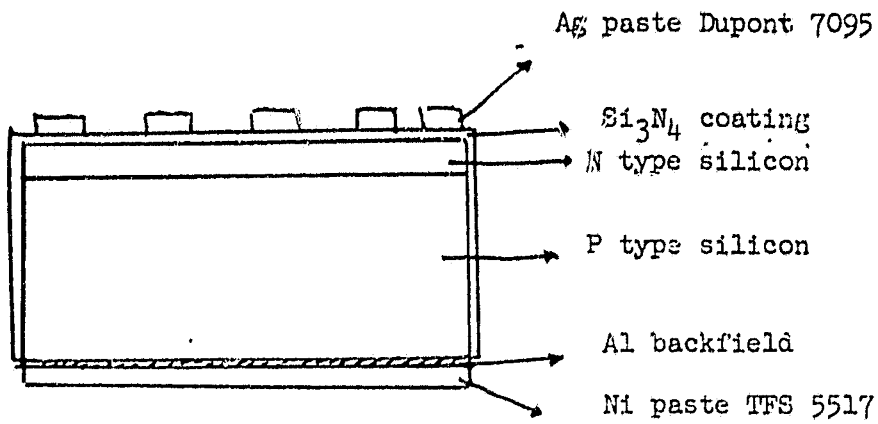

Fig. 7

SECTION 4.0

CONCLUSION AND RECOMMENDATION

The metallization of silicon solar cells coated with silicon nitride film and using thick film screenable ink was successful when Dupont Ag paste # 7095 was used on both sides of the cells.

The aluminum backfield was formed prior to the silver metallization using fritless Al ink (Electrink AFL - 40).

The metallization with commercial Ni pastes TFS # 5517, Cermalloy # 7028-5 and Sollos, Inc. experimental composition X-A was not successful in terms of the mechanical bond strength, solderability and electrical characteristics.

On the other hand, an addition of 10% Dupont Ag paste # 7095 to the Ni paste TFS # 5517 significantly improved the cell characteristics and it is recommended that further experiments should be done to optimize the mixing ratio.

It is further recommended to investigate the method of electroless Ni plating on the nitridized cells employing the following process sequence:

a: screening a resist on nitridized cells with the metallization pattern exposed

b: removing the nitride on exposed regions by H F

c: nickel plating followed by copper and/or tin plating

d: removing the mask